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Determination of Ten Acid Herbicides in Natural Waters

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DETERMINATION OF TEN ACID HERBICIDES IN NATURAL WATERS

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MANAGEMENT PERSPECTIVE

The technology transfer to Water Quality National Laboratory of a multi-residue method recently developed by Quality Assurance and Methods Section for the analysis of ten acid herbicides in water has been completed. The necessary equipment has been assembled in the WQNL, a chemist from the WQNL has been trained and the methodology has been validated on three types of waters from the Western and Northern Region. The transfer of this technology expands the capability of the WQNL as the existing methodology only analyzes five herbicides simultaneously rather than ten with the new scheme. The cost effectiveness of acid herbicide analyses is consequently increased significantly.

PERSPECTIVE-GESTION

La Section assurance de la qualité et méthodes a récemment mis au point une méthode multirésiduelle permettant d'analyser en même temps dix herbicides contenus dans l'eau. Les formalités de transfert de techniques au profit du Laboratoire national de la qualité des eaux sont terminées. Les appareils nécessaires ont été assemblés au LNQE; un chimiste du Laboratoire a été formé et on a vérifié la validité de la méthode en soumettant à des essais trois types d'échantillons d'eau provenant des Régions de l'Ouest et du Nord. Grâce à l'acquisition de cette nouvelle technique, le LNQE peut étendre son champ d'action, limité jusqu'ici par une méthode permettant uniquement d'analyser cinq herbicides à la fois. Il y a donc accroissement considérable de la rentabilité des analyses des herbicides acides.

ABSTRACT

An analytical method for the simultaneous determination of ten acid herbicides in natural water samples was developed by Quality Assurance and Methods Section (QAMS). This method has been successfully applied to three types of waters from Western Region by a chemist in Water Quality National Laboratory (WQNL). Recoveries of all ten acid herbicides from three types of fortified Western Regional waters were generally between 70 and 90% at 0.05 µg/L. This new method is superior to the existing methodologies since it not only combines two separate analyses into one but also extends the number of herbicides to ten.

RÉSUMÉ

La Section assurance de la qualité et méthodes (SAQM) vient de mettre au point une méthode analytique permettant de déceler en même temps dix herbicides acides contenus dans des échantillons d'eau naturelle. Un chimiste du Laboratoire national de la qualité des eaux (LNQE) a déjà appliqué avec succès la méthode lors de l'analyse de trois types d'échantillons d'eau provenant de la Région de l'Ouest. Le taux de dépistage des dix herbicides acides dans ces échantillons d'eau contaminée se situait en général entre 70 et 90 p. 100 à une concentration de 0,05 ug/l. Cette nouvelle méthode est plus efficace que celles qui existent déjà, car non seulement elle combine deux analyses différentes, mais elle permet également d'augmenter à dix le nombre d'herbicides analysés en même temps.

INTRODUCTION

In response to a request from the Western Water Quality Branch (Western and Northern Region), a multi-residue method for the analysis of ten acid herbicides in sediments (1) was developed in 1981 and later another method for the analysis of the same herbicides in natural waters (2) was also developed. The ten acid herbicides are: dicamba, MCPA, 2,4-DP, 2,3,6-TBA, 2,4-D, silvex, 2,4,5-T, MCPB, 2,4-DB and picloram. Currently, Water Quality National Laboratory analyzes five phenoxy acid herbicides, namely, 2,4-D, 2,4,5-T, 2,4-DB, 2,4-DP and MCPA, by the formation of methyl esters. Picloram is determined in a duplicate sample by 2-chloroethyl ester formation. This new multi-residue method (2) was developed to meet the immediate objective of enabling the simultaneous extraction and analysis of the ten acid herbicides in the same water sample thereby reducing sampling, transportation, storage and analytical costs. By the application of the modular concept in method development (3,4), the method was developed to meet a longer-term objective of generating a multi-class, multi-residue method in the future for the analysis of several types of trace organics in the same sample.

EXPERIMENTAL SECTION

Apparatus

See reference 1. For GC analysis of the final extracts, use a Hewlett-Packard 5880A GC (or equivalent) equipped with a split-splitless capillary column injection port, electron-capture detector and a 30 m x 0.25 mm i.d. SE-54 fused silica capillary column.

Reagents

See reference 1.

Method Optimization

The current methods in the Water Quality Branch Analytical Methods Manual (5) for herbicide analysis have certain limitations. Because of sensitivity problems, formation of methyl ester derivatives limits the application of the method to only a few di- and trichlorinated herbicides. Particularly, the methyl esters of MCPA and MCPB have very low ECD response compared to the same derivatives of other common acid herbicides. Formation of the 2-chloroethyl esters of MCPA and MCPB does not improve the sensitivities by much.

This newly developed method (2) using PFBBr reagent for derivatization enables the simultaneous analysis of ten acid herbicides because of distinguishable retention times and good sensitivity of the PFB ester derivatives. The inclusion of a high resolution fused silica capillary column in the final analysis further improves the quality of results in terms of identification and quantitation of the herbicide derivatives.

Method Validation

When the method was developed, distilled and natural water samples from Lake Ontario fortified at 1, 0.1 and 0.05 ug/L were analyzed in the validation steps. Precision and recovery data were reported (2).

In this technology transfer exercise, a chemist from WQNL was trained to set up the method. The entire validation process was repeated using both distilled water and natural water samples from Western Region. Similar precision and accuracy (recovery) values were generated by the WQNL chemist, thus providing further substantiation to the practical performance of this method. The validation data are summarized in the appendix.

Analysis of Samples

Forty-five fortified or blank distilled water and natural water samples were analyzed with the present method for the ten acid herbicides. In the case of natural water samples, samples from three different locations in the Western Region were used.

REFERENCES

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3. H.B. Lee and A.S.Y. Chau. J. Assoc. Off. Anal. Chem., 66, 651 (1983).
4. A.S.Y. Chau. "Modular concept in Method Research and Development. A case example for the development of a multi-residue method for trace organic analysis," presented to the Northeast Regional Section, AOAC, June, 1983.
5. Analytical Methods Manual, Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa, Canada, 1979.

APPENDIX

1. Recovery and precision of herbicide analysis in fortified XAD-2 water samples (% CV in brackets).

Fortification levels (µg/L)	1	0.1	0.05
No of replicates	6	6	6
Dicama	85.0	73.0 (8.4)	85.7 (1.9)
MCPA	96.0 (7.8)	96.7 (11.0)	193.2 (2.4)
2,4,DP	104.2 (11.3)	98.0 (8.3)	91.5 (2.4)
2,3,6-TBA	91.0 (9.2)	84.0 (7.2)	88.7 (4.0)
2,4-D	101.0 (11.9)	103.3 (6.6)	98.5 (1.7)
Silvex	108.0 (10.6)	94.7 (7.6)	92.0 (0)
2,4,5-T	106.0 (3.6)	124.2 (11.2)	95.8 (2.4)
MCPB	87.0 (12.2)	76.5 (11.7)	86.3 (2.8)
2,4-DB	88.8 (10.1)	79.8 (12.0)	87.5 (3.6)
Picloram	113.2 (14.2)	77.8 (16.0)	107.8 (15.9)

2. Recovery and precision of herbicide analysis in fortified natural water samples (% CV in brackets).

Water Type	I	I	I	II	III
Concentration (µg/L)	1.0	0.1	0.05	0.05	0.05
No. of replicates	6	6	6	3	3
Dicama	81.2 (5.0)	87.4 (4.4)	83.0 (3.1)	86.0 (4.0)	95.0 (1.8)
MCPA	96.2 (2.6)	96. (11.0)	80.0 (5.6)	77.0 (0)	64. (13.5)
2,4,DP	99.4 (3.3)	84.2 (8.0)	88.7 (3.2)	78.5 (6.3)	76. (10.2)
2,3,6-TBA	96.0 (2.1)	80.2 (4.6)	88.2 (3.2)	76.3 (7.6)	78.3 (5.8)
2,4-D	99.6 (3.9)	94.8(11.0)	91.8 (7.1)	88.0 (2.0)	85.3 (4.7)
Silvex	103.6 (5.0)	86.0 (7.2)	80.8 (6.9)	91.7 (3.1)	93.7 (24)
2,4,5-T	109.0 (5.5)	105.0 (4.3)	87.2 (3.0)	86.7 (3.3)	90.7 (7.0)
MCPB	98.0 (4.8)	83.0(11.0)	72.8 (5.7)	93.0 (0)	89.0 (1.9)
2,4-DB	92.8 (5.1)	84.2(14.0)	73.2 (8.1)	67.7 (3.4)	111.7 (4.1)
Picloram	69.5 (8.8)	77.8(10.5)	68.7 (8.3)	99.7 (7.7)	93.6 (4.3)

DETECTION LIMITS AND TMU FOR ACID HERBICIDES USING DIFFERENT METHODS

METHYL ESTERS	DETECTION LIMIT (ppb)	TMU
MCPA	0.2	5 HOURS
2, 4-DP	0.004	
2, 4-D	0.004	
SILVEX	0.004	
2, 4, 5-T	0.002	
2, 4-DB	0.009	
2-CHLORO-ETHYL ESTER		
PICLORAM	0.2	5 HOURS
PFB ESTERS		
DICAMBA	0.05	5 HOURS
MCPA	0.05	
2, 4-DP	0.05	
2, 3, 6-TBA	0.05	
2, 4-D	0.05	
SILVEX	0.05	
2, 4, 5-T	0.10	
MCPB	0.10	
2, 4-DB	0.10	
PICLORAM	0.10	

TMU= Time required to analyze one water sample